

Supporting Information

Synthesis, characterization, and highly acid-resistant properties of crosslinking β -chitosan with polyamines for heavy metal ion adsorption

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Syntheses and Characterization

Analyses by UV-Vis spectrometer

Fig. S1 shows the UV-Vis analyses of the synthesized graft-modified chitosan and its intermediate products, and the following results can be drawn from the figure. After the Schiff base benzene ring mono-substitution reaction to form BCS, the benzene ring became a strong chromophore with an absorption intensity of 0.95 for ultraviolet absorption, and the area between 250 nm and 300 nm wavelength is a strong absorption area. After the epoxide groups were introduced, the spectrum showed no significant changes as the epoxide groups did not have a significant absorption intensity for ultraviolet. The introduced polyamine has double-bonded alkene and C-N groups, and the auxochrome groups have a lower absorption intensity for ultraviolet than the benzene ring strong chromophores, thus this absorption band showed no significant changes from 250 nm to 300 nm. Finally, after the removal of protecting groups, as the benzene ring strong chromophores were removed, the absorption intensity of these molecules for ultraviolet was not shielded by that of benzene rings, and the absorption intensity of these molecules for ultraviolet declined to around 0.80, proving that the modification of chitosan was successful by introducing polyamine for crosslinking.

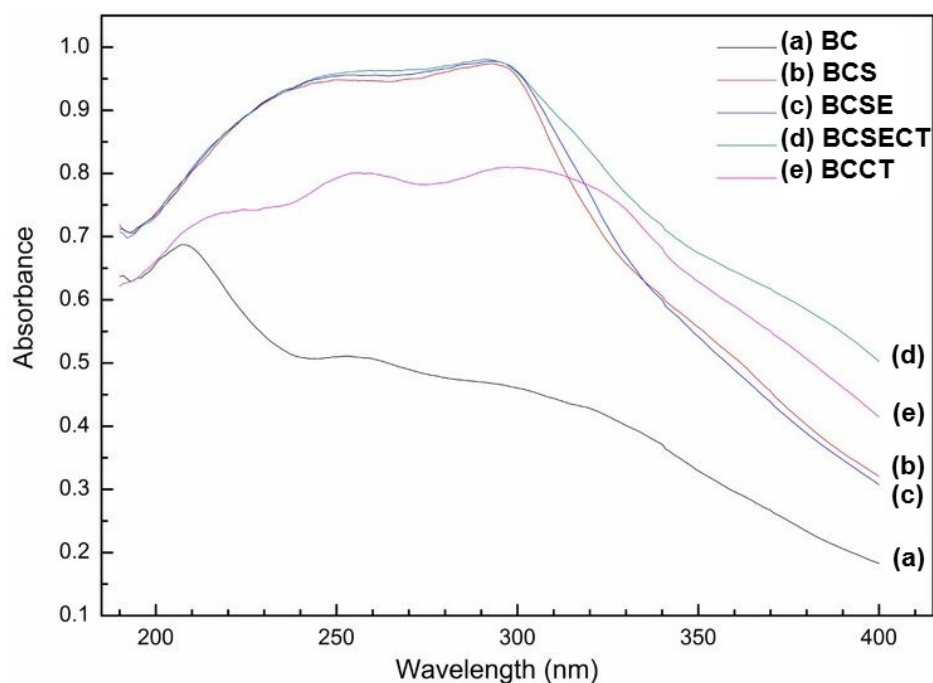


Fig. S1 UV-Vis analyses of the synthesized graft-modified chitosan and its intermediate products.

Analyses by X-ray powder diffractometer

Fig. S2 shows the analyses by X-ray powder diffractometer. BC shows a strong derivative peak at $2\theta = 20^\circ$, namely, a characteristic peak of chitosan. For BCS, a new derivative peak was generated at $2\theta = 6^\circ$ after β -chitosan reacted with benzaldehyde, and the signal of the derivative peak at $2\theta = 20^\circ$ intensified, proving that benzaldehyde was successfully introduced to β -chitosan molecules with the generation of protecting groups. After BCSE reacted with epichlorohydrin and the epoxide groups were introduced, the signal of the derivative peak at $2\theta = 20^\circ$ weakened, indicating that epoxide groups can reduce crystallinity of chitosan. After the ring opening and crosslinking of BCSECT with triethylenetetramine, the signal peak did not show any significant change. After the benzene ring mono-substituted amine groups were removed from BCCT, the derivative peak at $2\theta = 6^\circ$ disappeared, indicating that these groups were removed from the molecular structure successfully. In addition, the signal of the derivative peak at $2\theta = 20^\circ$ intensified, indicating that the hydrogen bond force intensified after crosslinking.

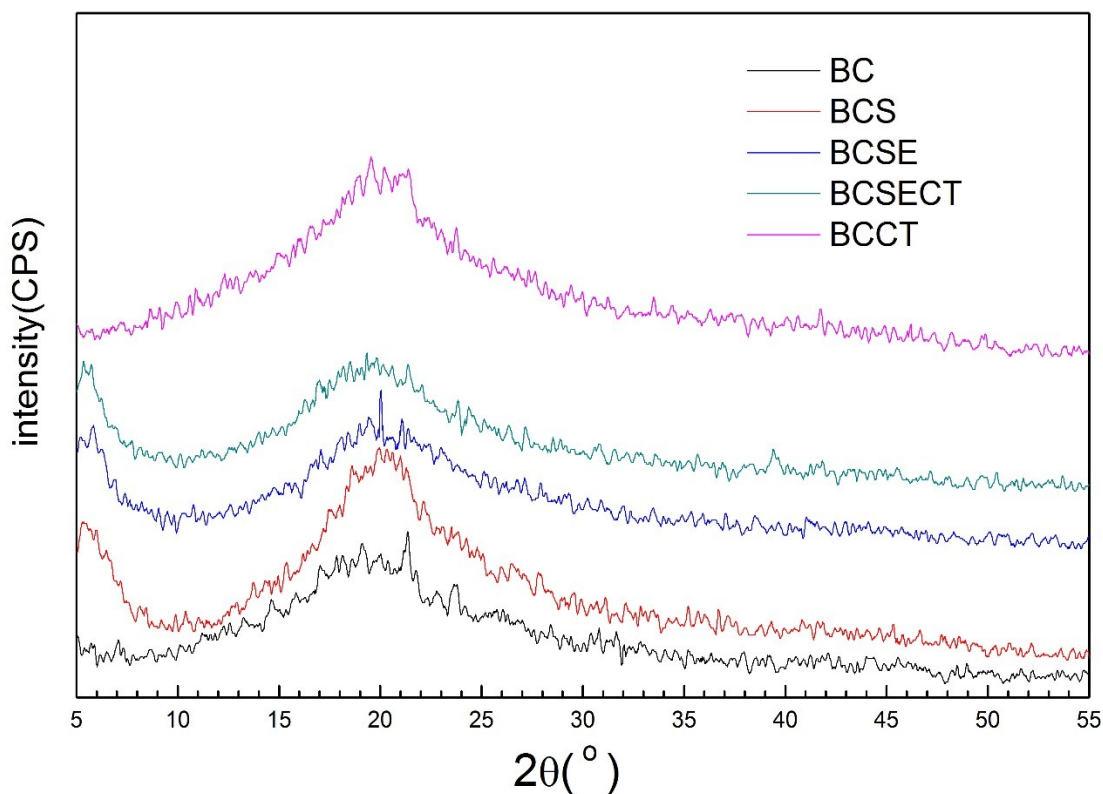


Fig. S2 XRD of graft-modified chitosan and its intermediate products.

Analyses by solid state nuclear magnetic resonance spectrometer

Fig. S3 shows the analyses by solid state nuclear magnetic resonance spectrometer. The relative intensity of (C3, C5) and (C1) was different before and after modification, indicating that the molecular structure was also different. The signal of the wave crest at (C6, C2) intensified after modification, meaning that polyamine was successfully introduced to C6-OH for crosslinking. The wave crest signal at (C3, C5) intensified, indicating that it was possibly because C3-OH could have the chance to be involved in part of the crosslinking reaction in the three-dimensional space as C2- was crosslinked with amine protecting groups, and the wave crest signals at (C4) and (C1) intensified, which was caused by the change of the chemical environments where the two carbon atoms are located.

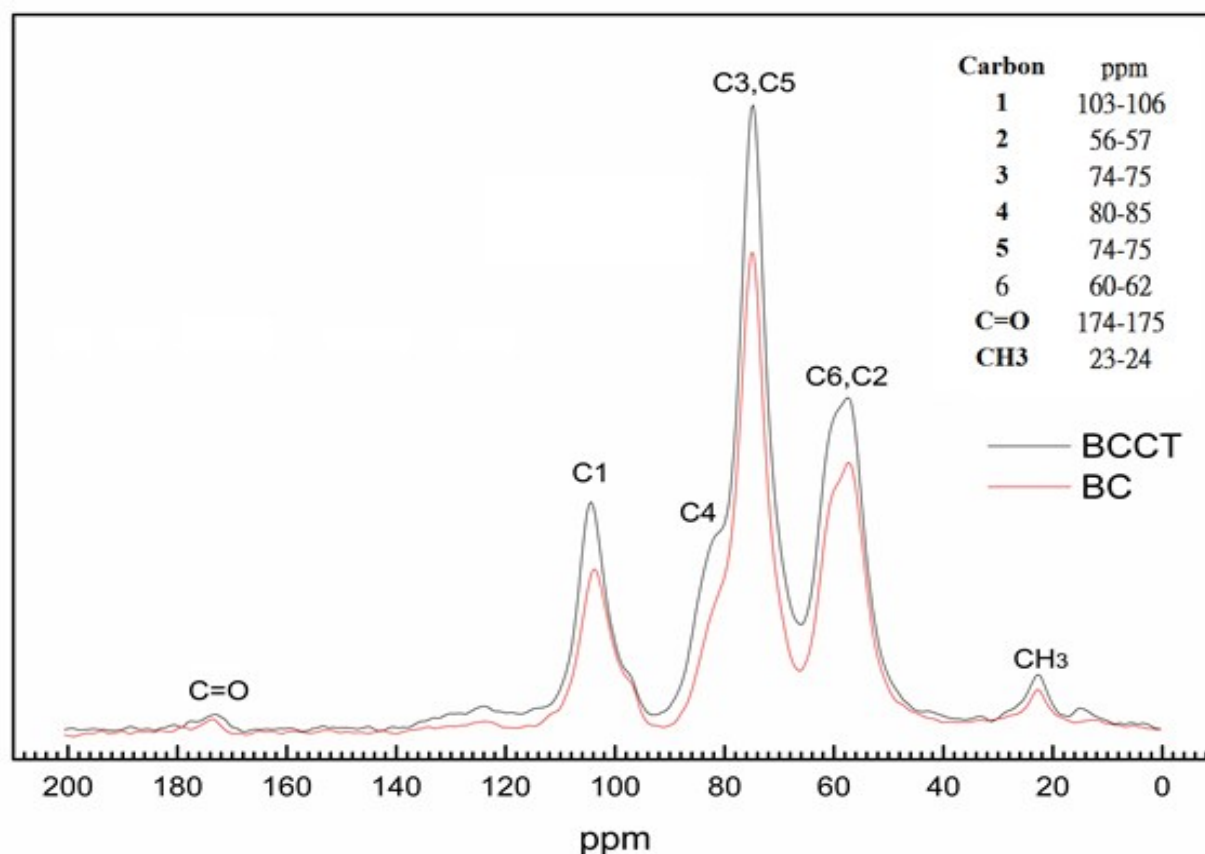


Fig. S3 ^{13}C solid state NMR CP/MAS mapping of chitosan before and after modification.

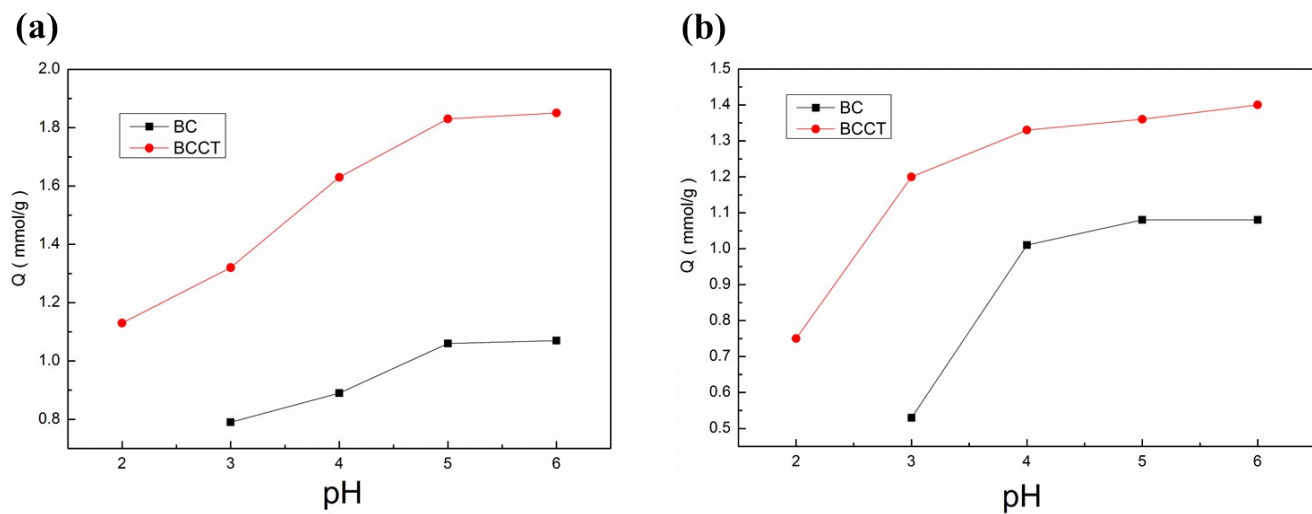


Fig. S4 Adsorption capacities of chitosan for (a) copper ions and (b) silver ions before and after modification.

Table S1. Surface area and porosity of β -chitosan before and after modification.

Sample	BC	BCCT
Single point surface area at $P/P_0 = 0.200909858$	0.6921 m ² /g	0.1372 m ² /g
BET surface area	0.6894 m ² /g	0.1176 m ² /g
Langmuir surface area	0.9278 m ² /g	0.1439 m ² /g